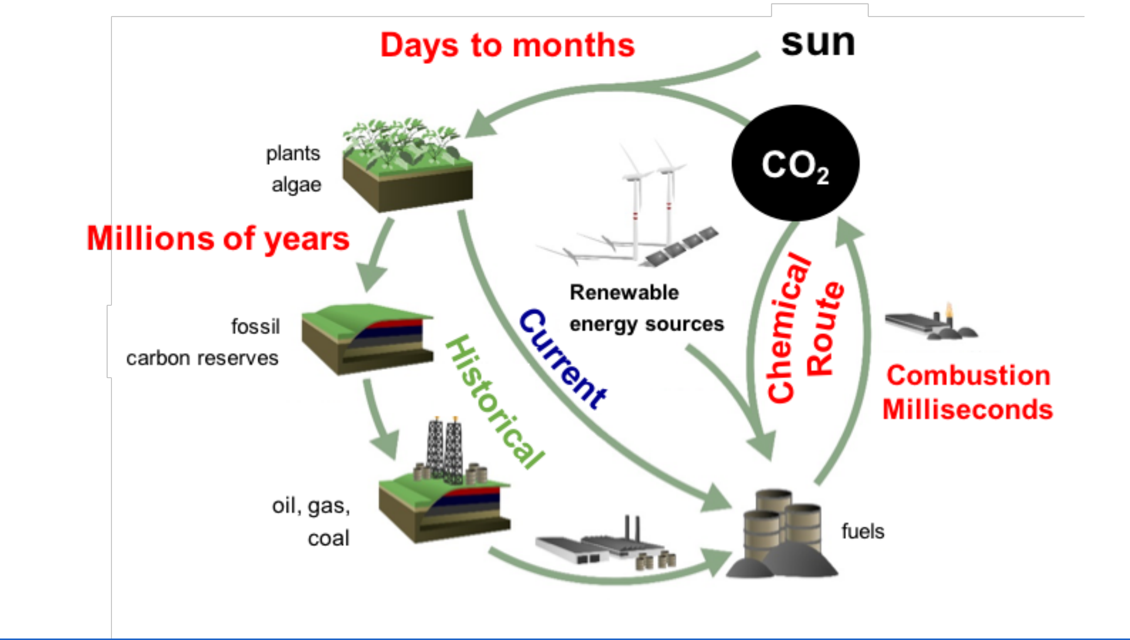
FACULTY OF ENGINEERING AND ARCHITECTURE

Catalyzing a CO_2-neutral Society

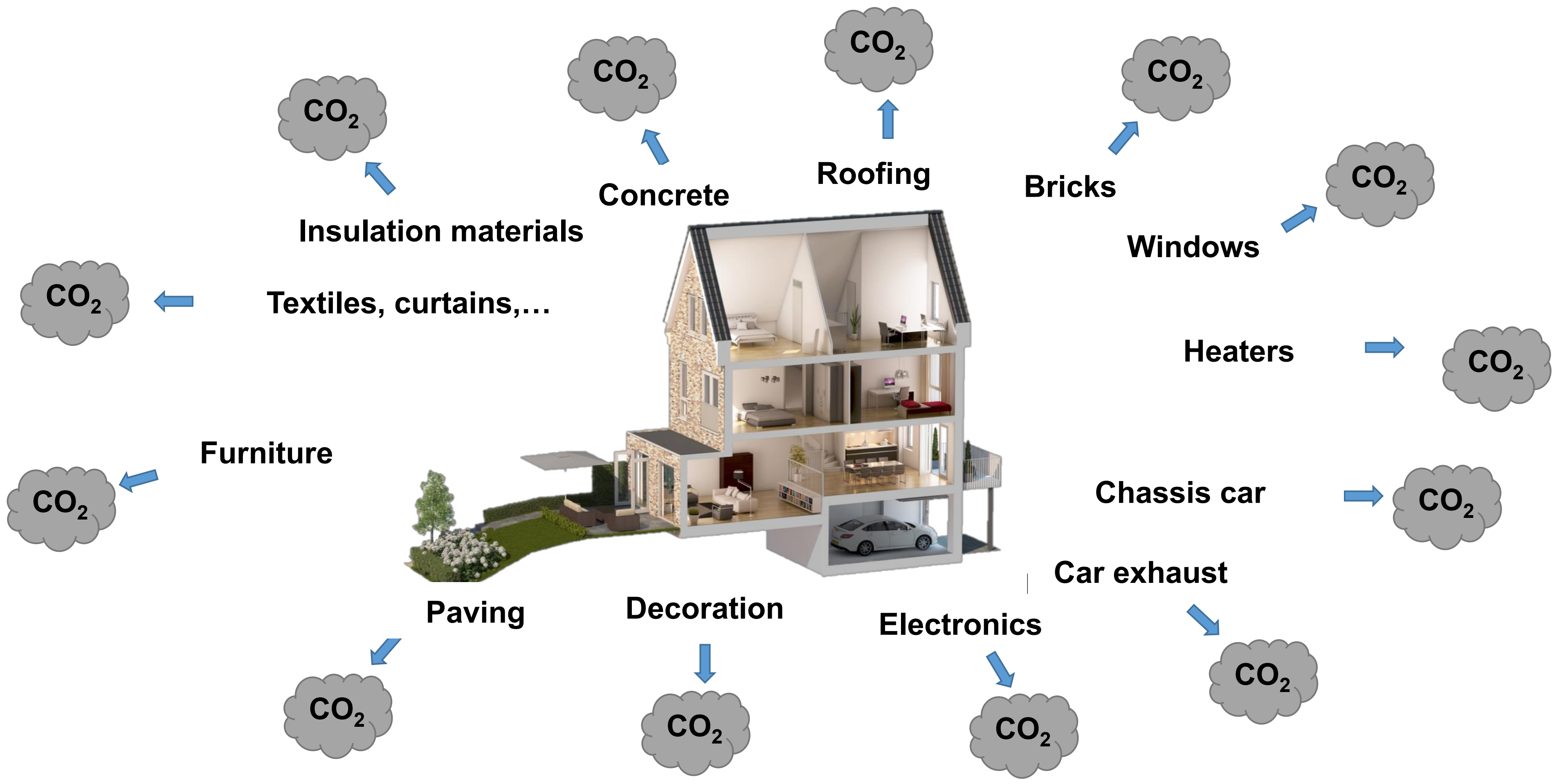


Cesar A. Urbina Blanco and Mark Saeys, Laboratory for Chemical Technology, Ghent University

GHENT UNIVERSITY

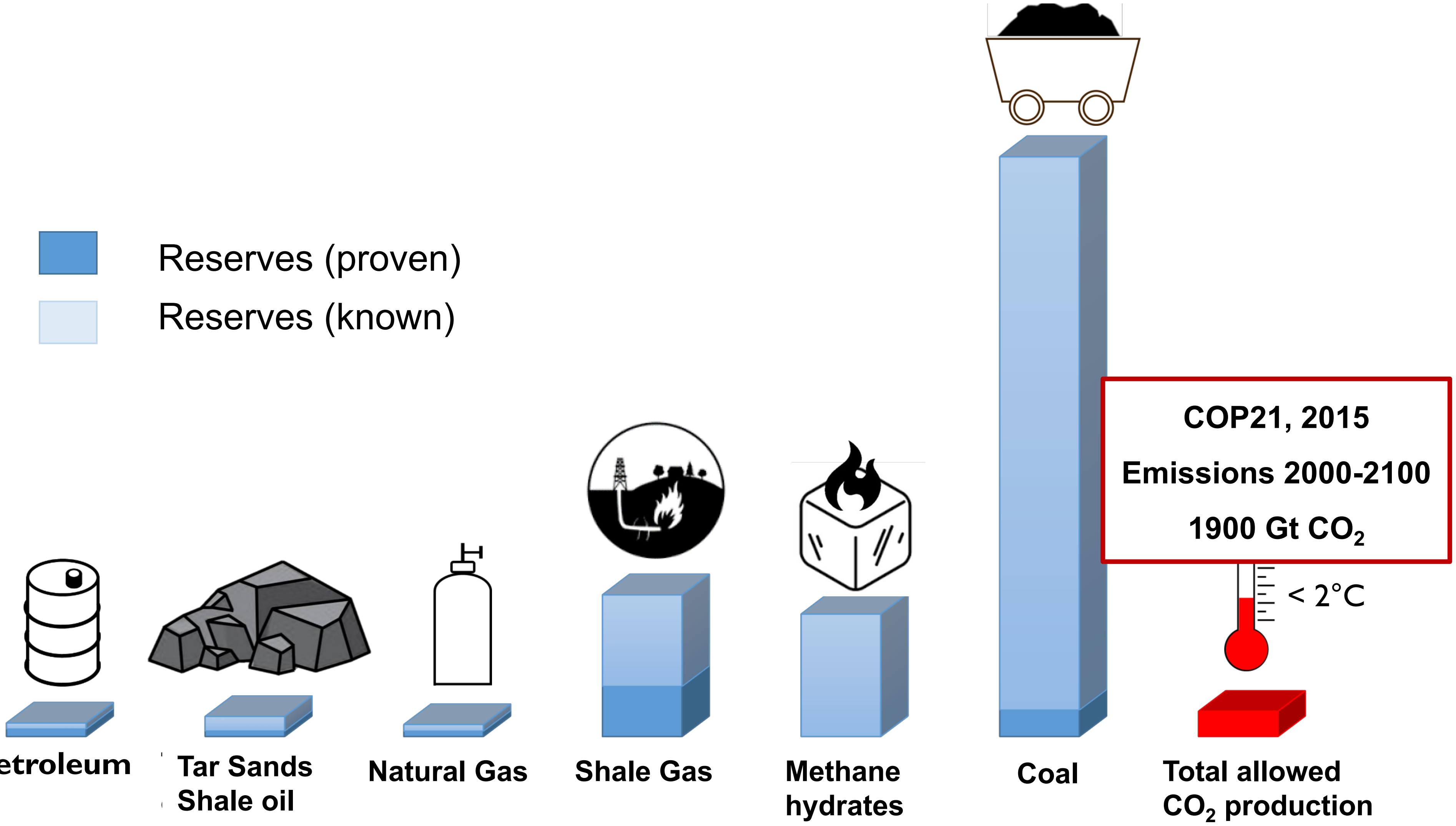
De Koninklijke Vlaamse Academie van België voor Wetenschappen en Kunsten

Carbon-based Society



GHENT
UNIVERSITY

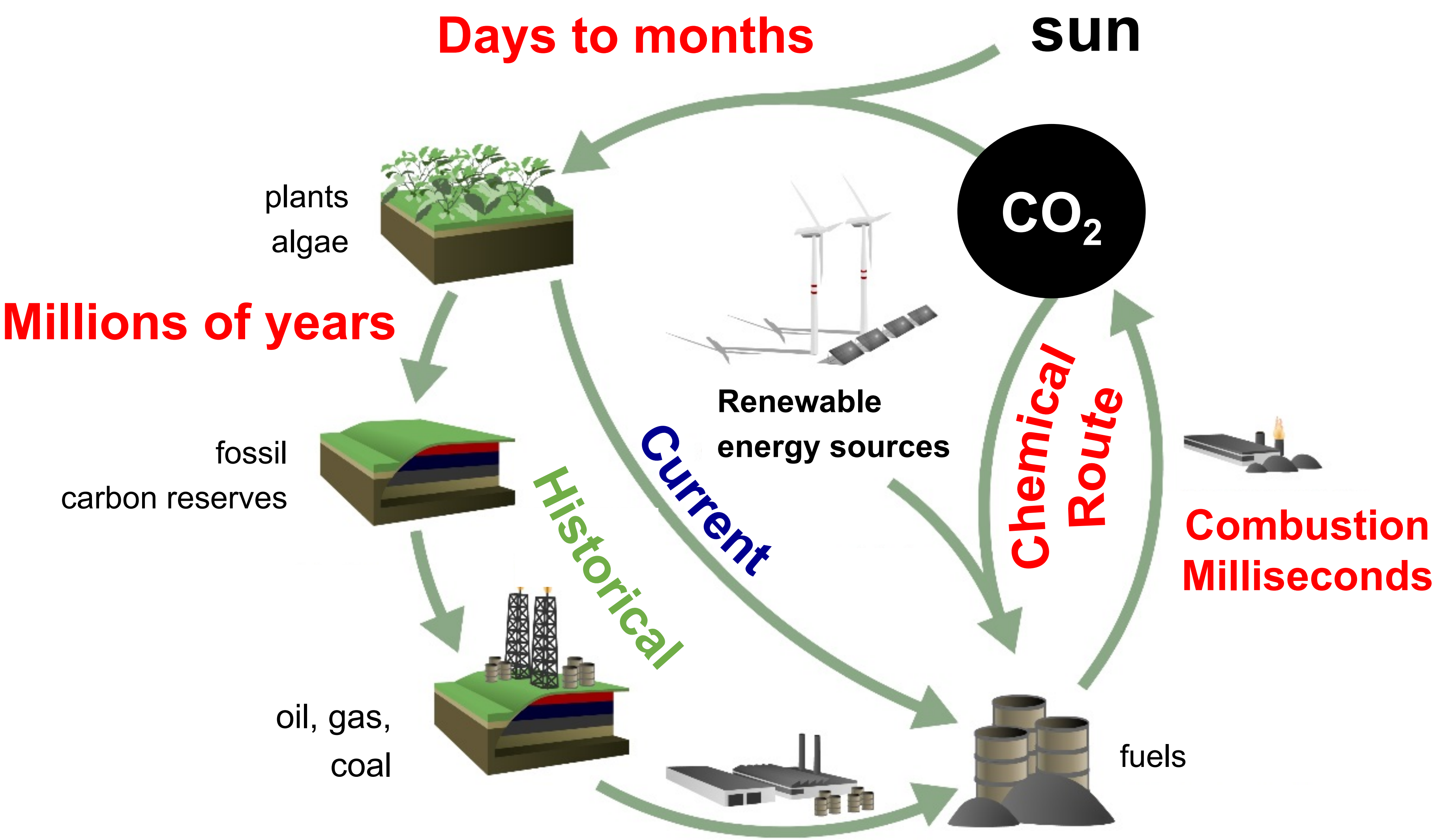
Fossil Carbon Reserves



Martens et al. KVAB Standpunt 39

GHENT UNIVERSITY

CO_2 Cycle: Kinetic challenge



GHENT UNIVERSITY

Europe: CCU high on the agenda

EUROPEAN COMMISSION

RTD - Energy

ENER - Renewables, R&I, Energy Efficiency
JRC – Institute for Energy and Transport

Renewing efforts to **demonstrate** CCS in the EU and **developing sustainable CCU**

By 2020:
- At least one commercial-scale CCS
- Completed feasibility studies for use of captured CO_2 for **fuels and value added chemicals**;
- At least **4 pilots** for production of value added chemicals from captured CO_2;

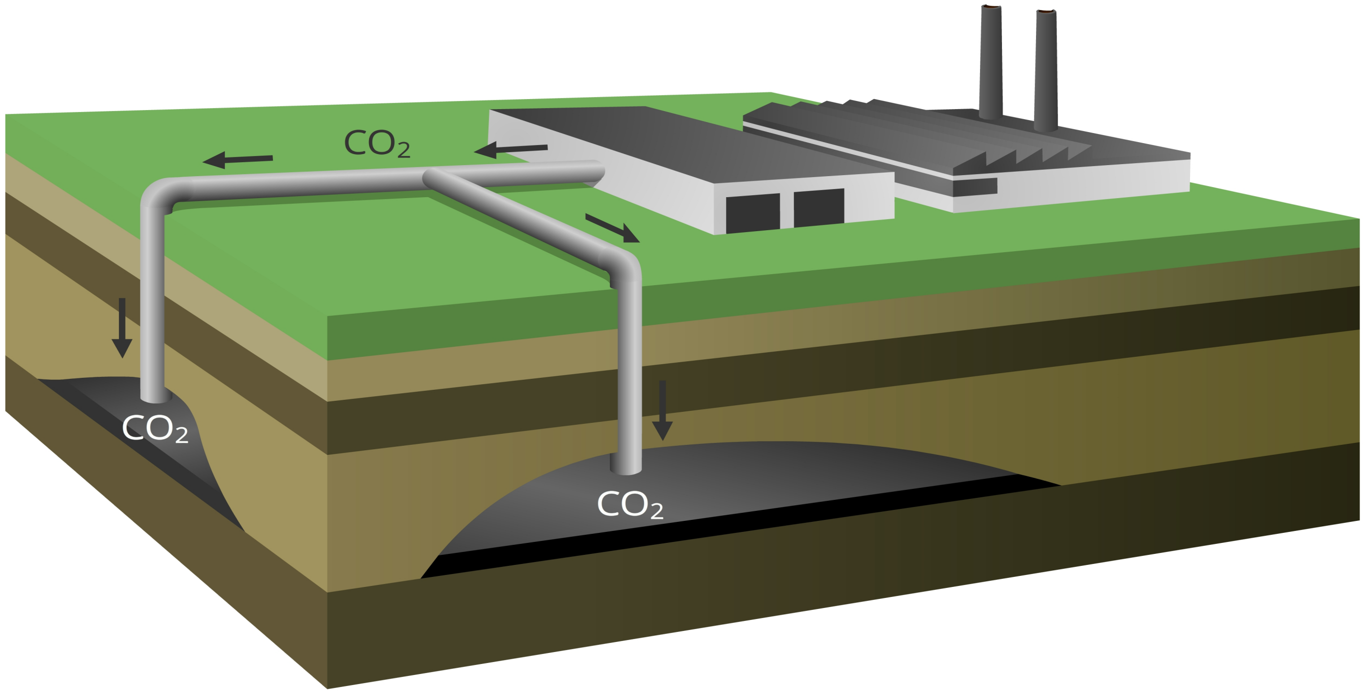
On the road to 2030:
- Further develop the potential of the industrial use of captured CO_2

Ref: SET Plan Secretariat – 05 April 2016

GHENT UNIVERSITY

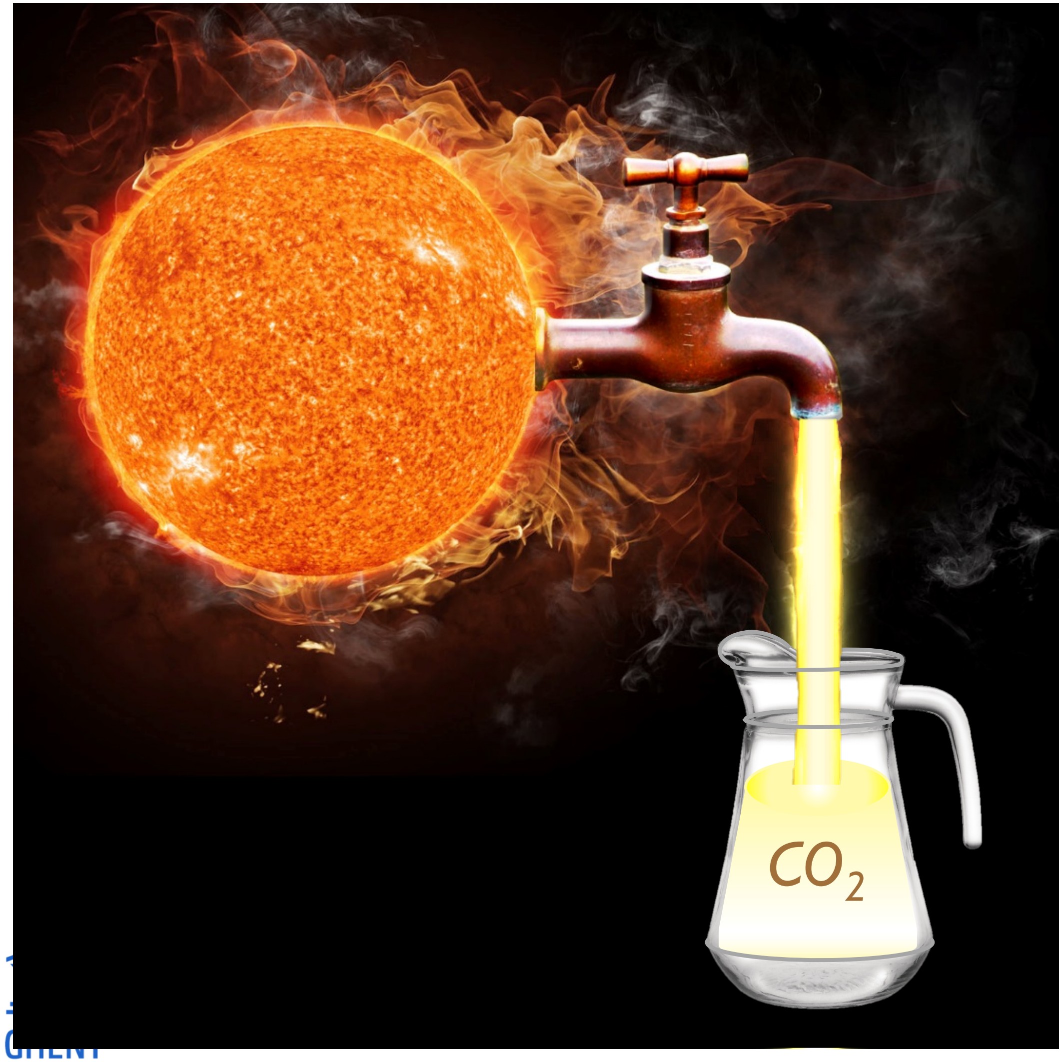
Capture and Storage

CCS: CO_2 produced at point sources is captured and sequestered in depleted oil and gas reservoirs



GHENT UNIVERSITY

Storage of Solar Photons



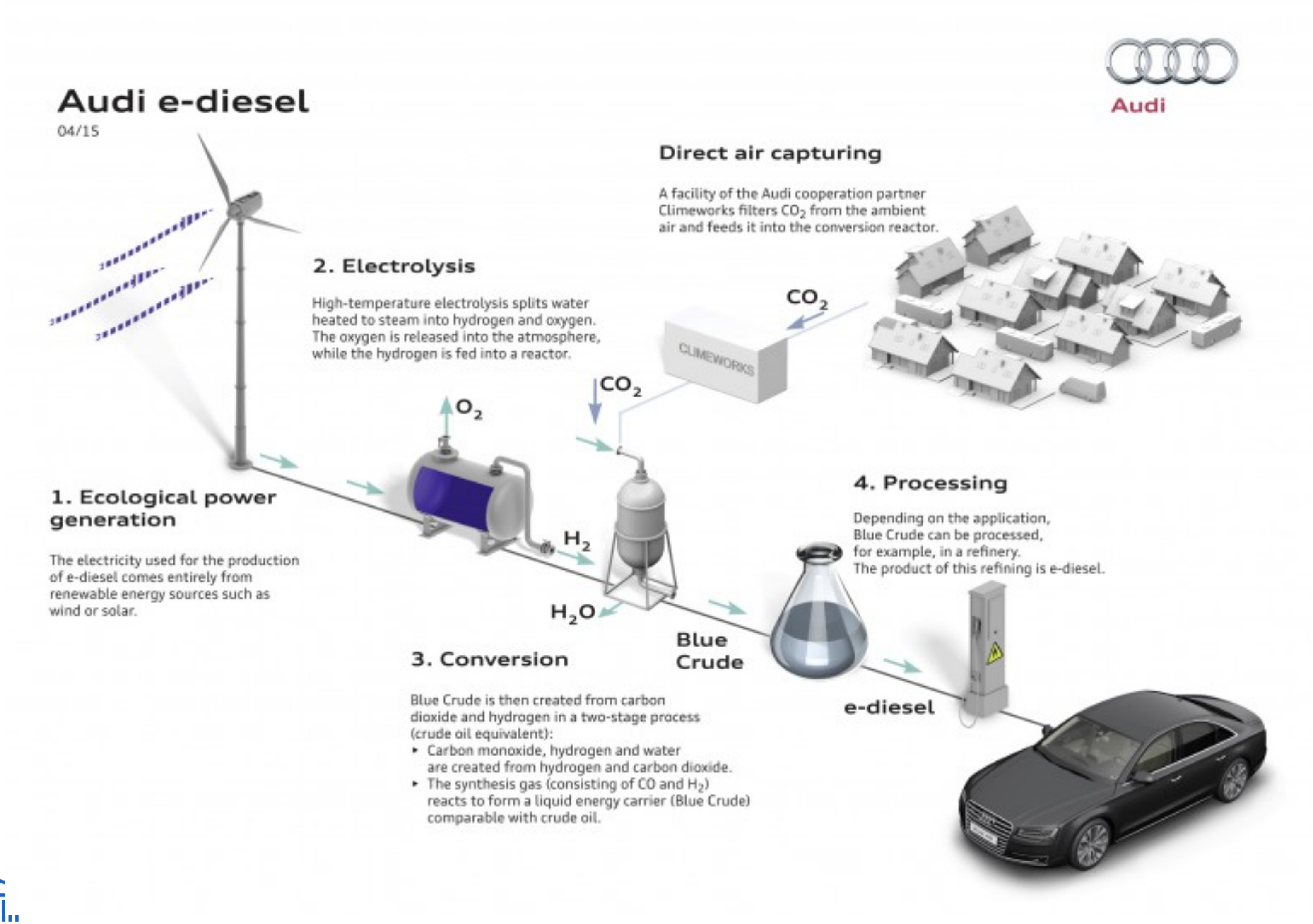
SOLAR ENERGY + CO_2 + H_2O

↓ CATALYSIS

SOLAR FUELS
SOLAR MATERIALS

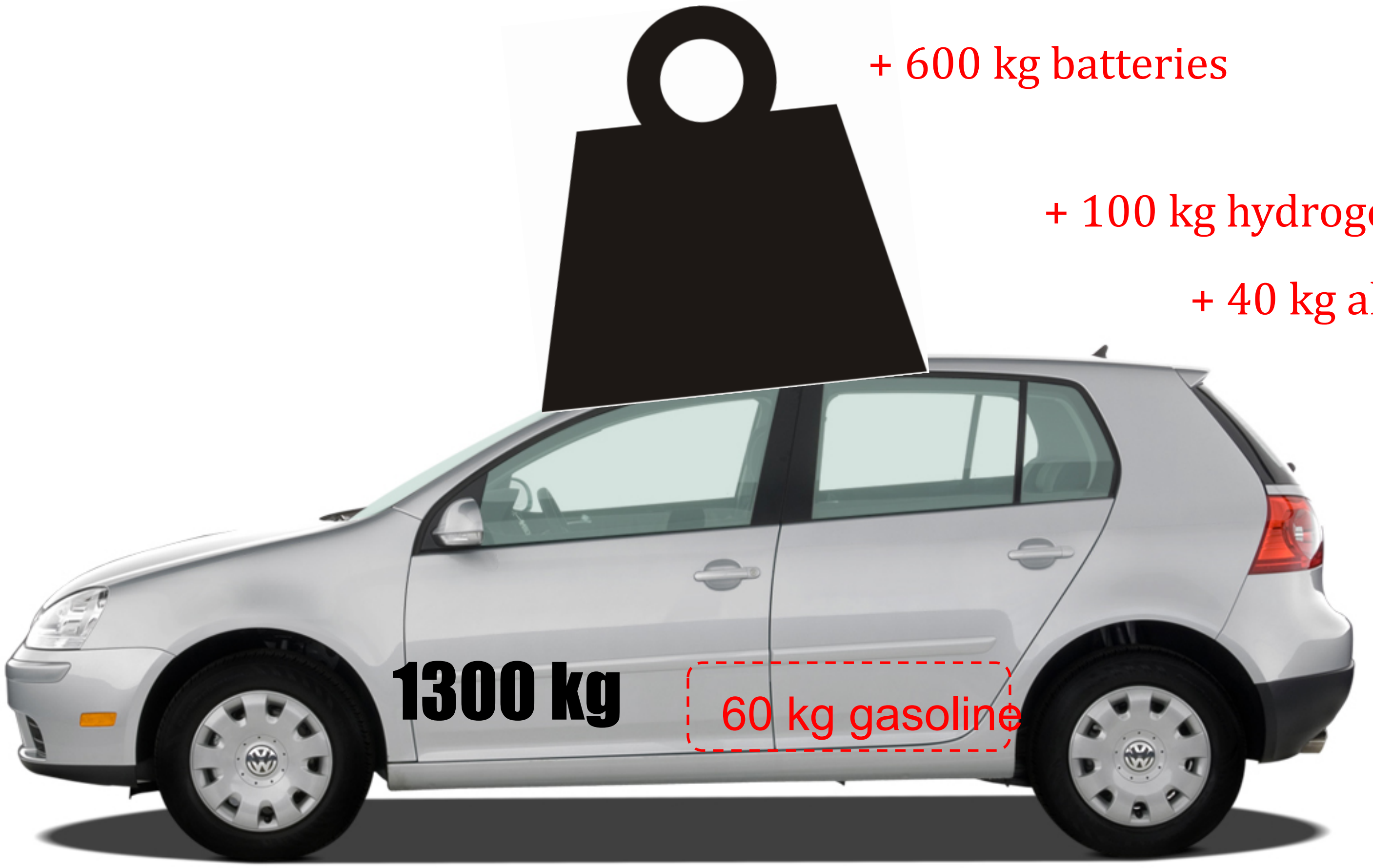
Molecule	Heat (kJ/mol C)	H_2 eq.	Fraction H_2 energy stored
Hydrogen	-240		100
Methanol	-680	3	94
Diesel	-640	3	89
Glucose	-450	2	94

Storage of Solar Photons: Audi and Sunfire



GHENT UNIVERSITY

Liquid fuels: Convenient, High energy-density



Power	13 kWh/kg gasoline x 0.5 kg/s ~ 25 MW
Energy	50 kg gasoline = 2.3 GJ
Solar?	1.4 kW/m^2 -> 460 hours on 1 m^2 for 2.3 GJ
Electrical?	Power plant ~ 500 MW

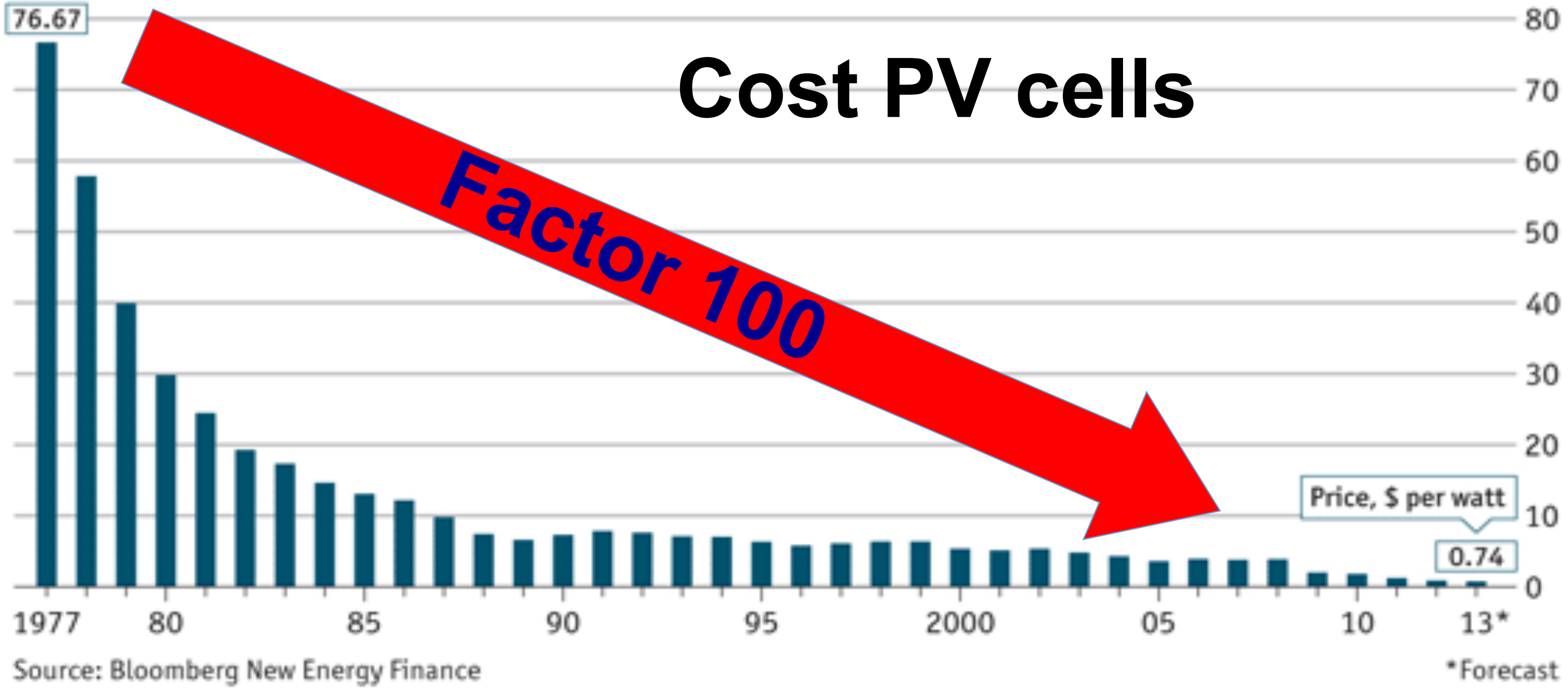
GHENT UNIVERSITY

Rakesh Agrawal, Purdue

Cost of Solar Fuels (€/liter)

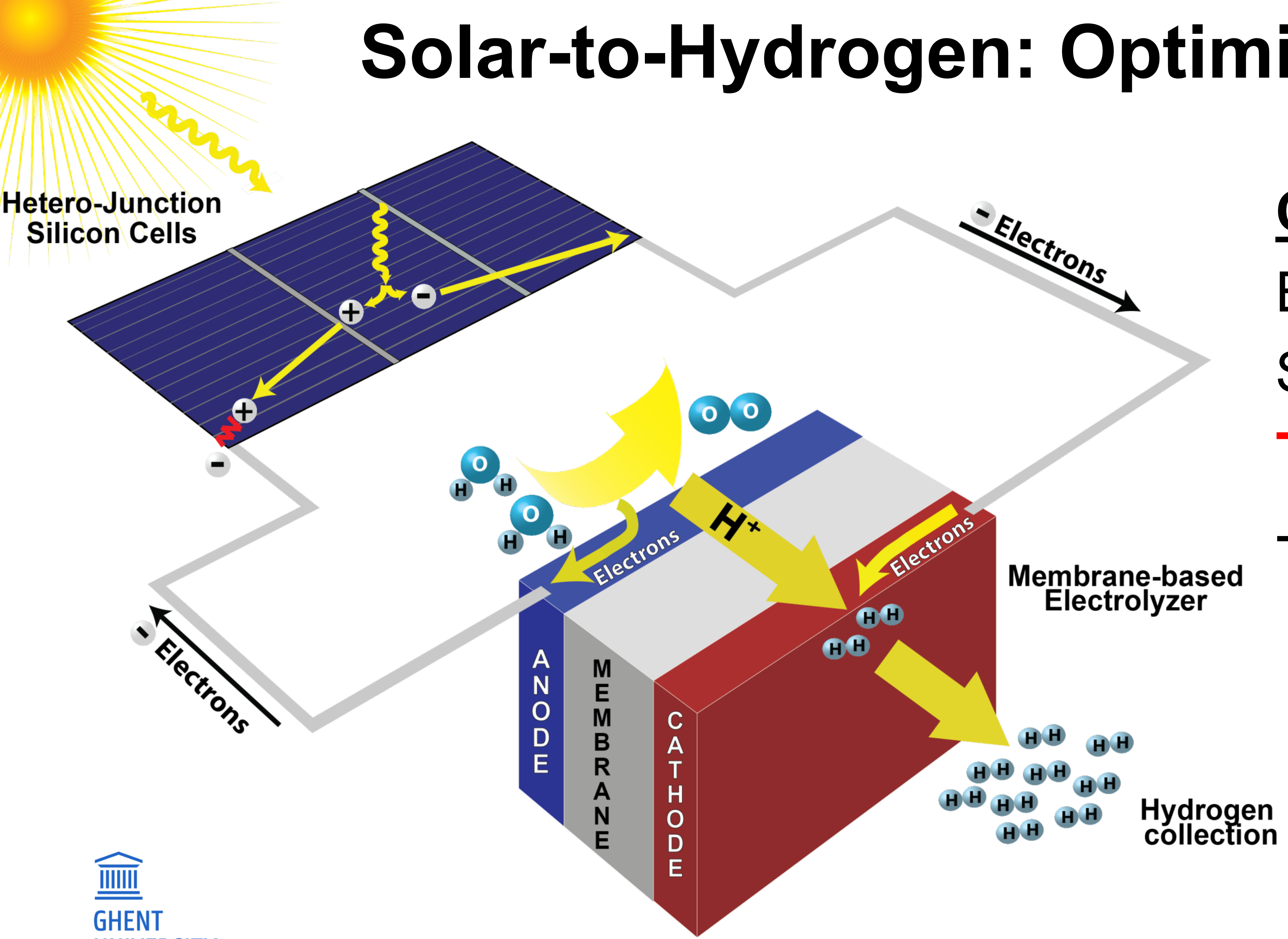
Market price	**0.22**
Electricity at 0.10 €/kWh	1.10
Electricity at **0.01 €/kWh**	**0.24**

European Commission, 2016



GHENT UNIVERSITY

Solar-to-Hydrogen: Optimistic study



Cost of materials

Electrolyser: 10%

Si PV: 90%

Total: 0.75 €/kg H_2

-> 0.15 €/l solar fuel

GHENT UNIVERSITY

Modestino et al., Ener. Env. Sci., **2014**

Solar fuels and Batteries: Energy Storage

Energy density:
Li-ion battery: 200-500 kWh/m^3
Liquid fuels: 4,000-10,000 kWh/m^3

Life time:
Battery: 10-20 years

Levelized **cost** for battery storage:
\$0.8-1.0/kWh -> \$0.2/kWh (\$250/kWh capacity)

Levelized **cost** for H_2 production:
\$2-4/kg H_2 or \$0.05-0.1/kWh

Gasoline: \$1.0/l or \$0.1/kWh

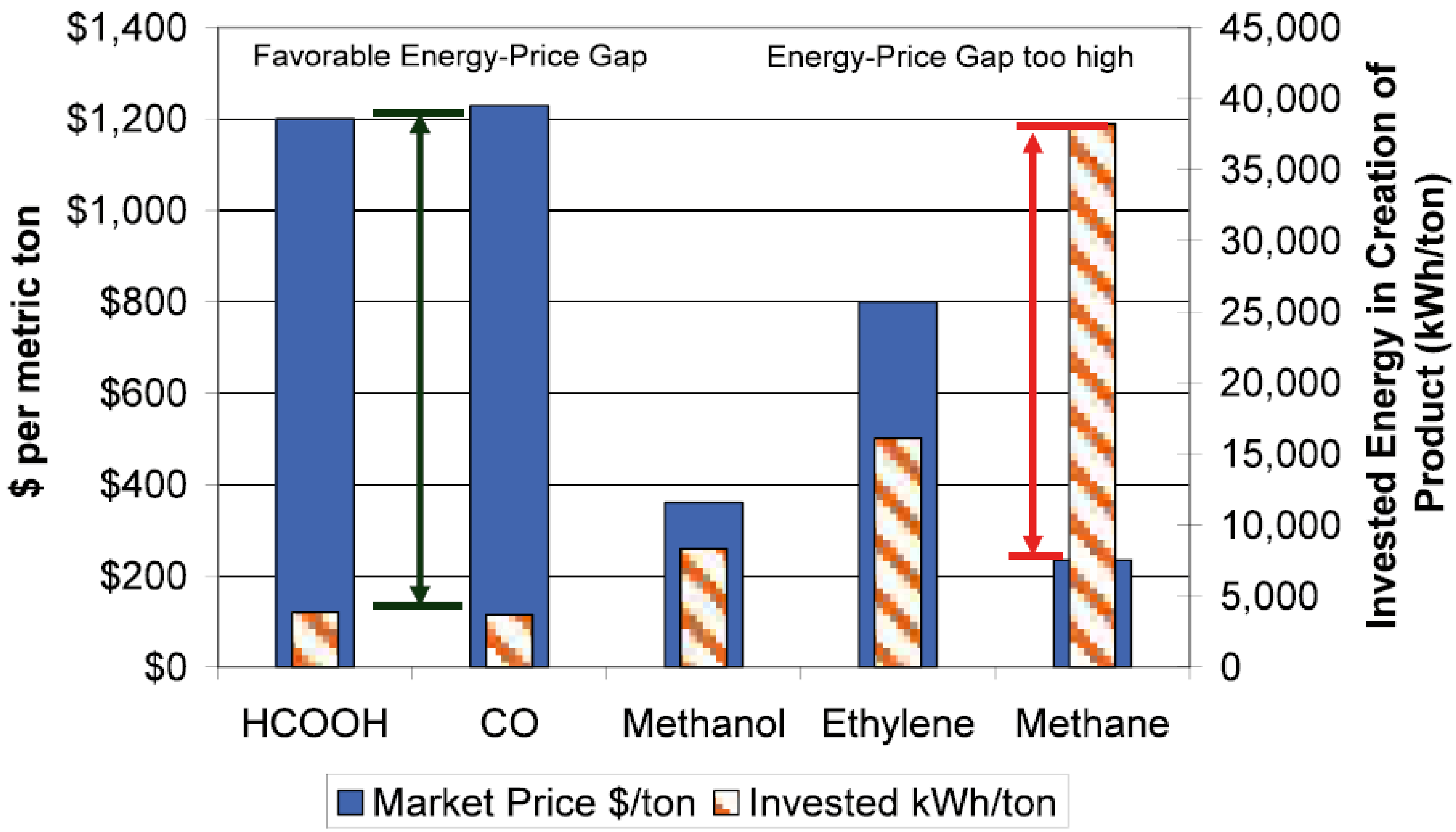
World's largest battery, Ni-Cd
40 MW for 7 min

Tesla ~70,000 Euro

GHENT UNIVERSITY

Lewis, Science, 2016, Research opportunities to advance solar energy utilization

Energy-Price Gap of CO_2-based products



GHENT UNIVERSITY

Det Norske Veritas (2011) "Carbon Dioxide Utilization Electrochemical Conversion of CO_2-Opportunities and Challenges"

Formic Acid – Current Industrial Route

1) $CO_{(g)} + CH_3OH_{(l)} \rightleftharpoons HCOOCH_{3(l)}$ (30%)

2) $HCOOCH_{3(l)} + H_2O_{(l)} \rightleftharpoons \mathbf{HCOOH_{(l)}} + CH_3OH_{(l)}$

- ✔ No byproduct formation
- ! Volatile intermediate
  FA catalyzes reesterification
- ✖ Equilibrium limited
  Favored by dilution

GHENT UNIVERSITY

Formic Acid – Catalytic route

Formic Acid Synthesis	$CO_2(g) + H_2(g) \rightleftharpoons HCOOH(l)$	$\Delta G^\circ_{298} = +39.9$ kJ/mol
Formate Synthesis	$CO_2(aq) + H_2(g) + NH_3(aq) \rightleftharpoons HCOO^-(aq) + NH_4^+(aq)$	$\Delta G^\circ_{298} = -35.4$ kJ/mol

- 100% atom efficient
- Economically-feasible
- Growing market

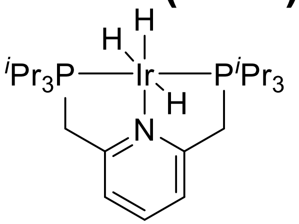
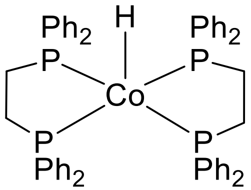
- Stoichiometric base required
- Small market 620 kton/year

- Catalysts recycling

GHENT UNIVERSITY

Formic Acid – Catalytic route

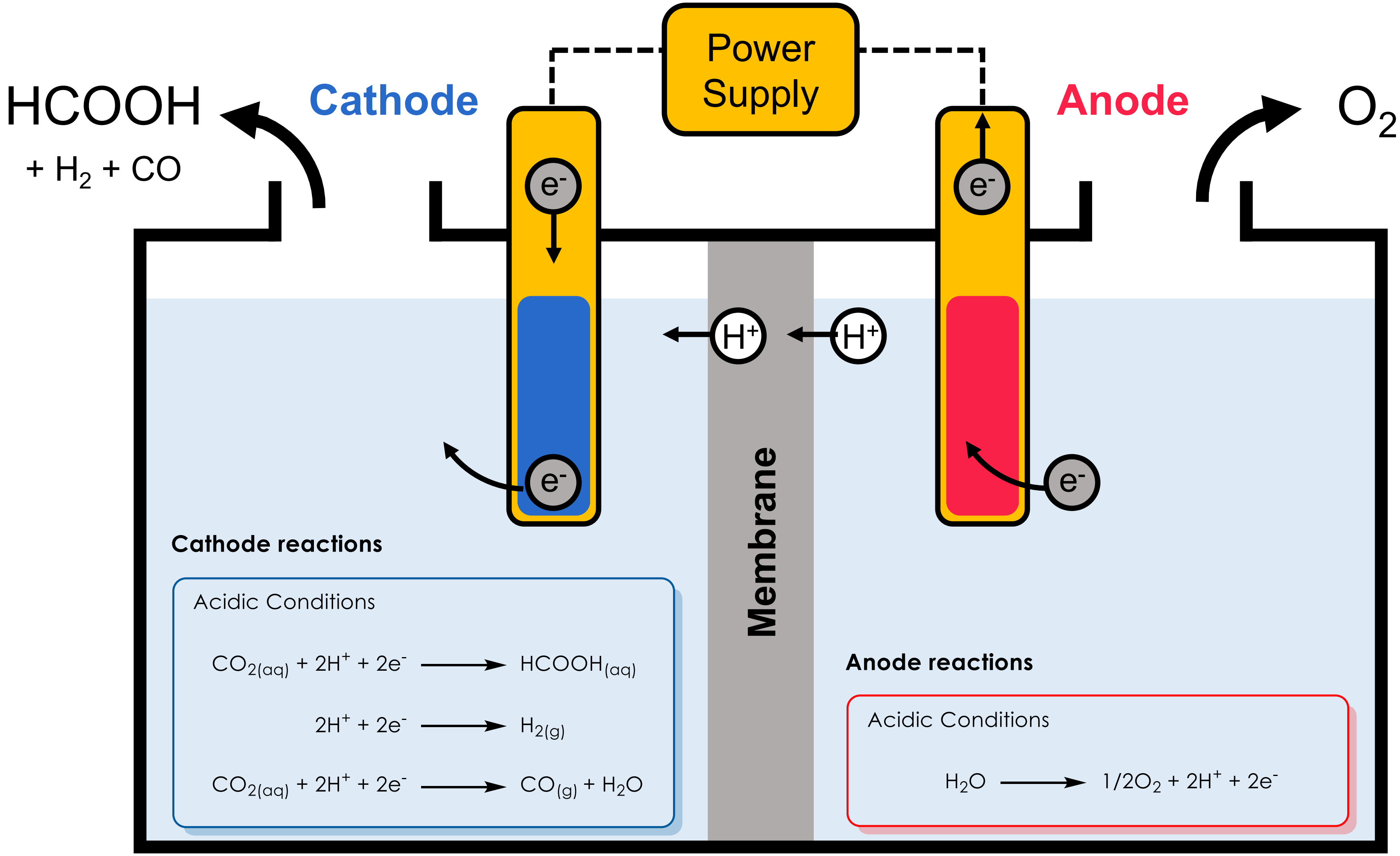
$$CO_2(aq) + H_2(g) + Base(aq) \rightleftharpoons HCOO^-(aq) + HBase^+(aq)$$

Catalyst	Solvent	Base	$P(H_2/CO_2)$ (MPa)	T (° C)	Time (h)	TON	TOF (h^{-1})
Nozaki (2009)[a] 	H_2O/ THF	KOH	4/4	200	2	300000	150000
			4/4	120	48	3500000	73000
Linehan (2013)[b] 	THF	Verkade's base	0.05/0.05	21	1	3400	3400
			1/1	21	<1	9400	74000
Mori and Yamashita (2017) Ru/LDH (Mg^{2+}/Al^{3+} = 5)	H_2O	KOH	1/1	100	24		29

[a] Tanaka, R.; Yamashita, M.; Nozaki, K. *J. Am. Chem. Soc.* **2009,** *131* (40), 14168-14169.
[b] Jeletic, M. S.; Mock, M. T.; Appel, A. M.; Linehan, J. C. *J. Am. Chem. Soc.* **2013,** *135* (31), 11533-11536.
[c] Mori, K.; Taga, T.; Yamashita, H. *ACS Catal.* **2017,** *7* (5), 3147-3151.

Formic Acid – Electrochemical route

$$CO_{2(aq)} + H_2O \rightleftharpoons HCOOH(aq) + 1/2\, O_2(g)$$



Sn-based electrodes

Economically-feasible

Up to 94% Selectivity

Early stage

Low catalysts stability

Methanol synthesis

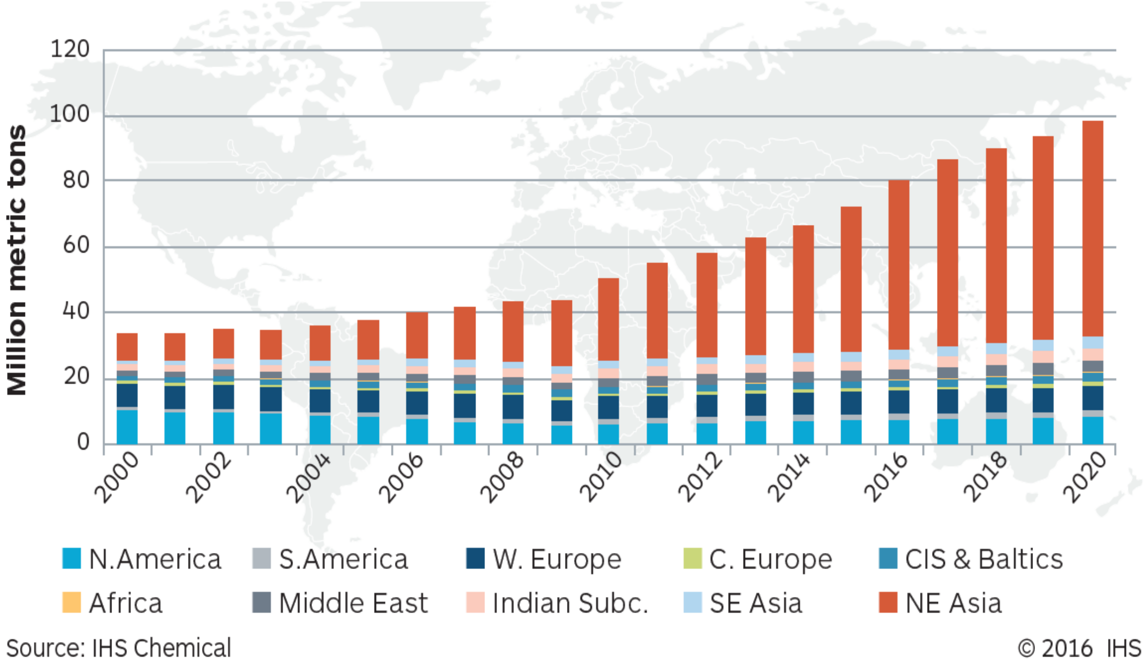
Methanol Synthesis

(1) $CO + 2H_2 \rightleftharpoons CH_3OH$ $\Delta H°_{298}$ = -91 kJ/mol $\Delta G°_{298}$ = -25 kJ/mol

(2) $CO_2 + 3H_2 \rightleftharpoons CH_3OH + H_2O$ $\Delta H°_{298}$ = -50 kJ/mol $\Delta G°_{298}$ = +4 kJ/mol

- Direct use as fuel
- 45% “power to power” efficiency[a]
- Economically-feasible
- Large market
- Green Premium

- High energy consumption
- Thermodynamically limited



GHENT UNIVERSITY

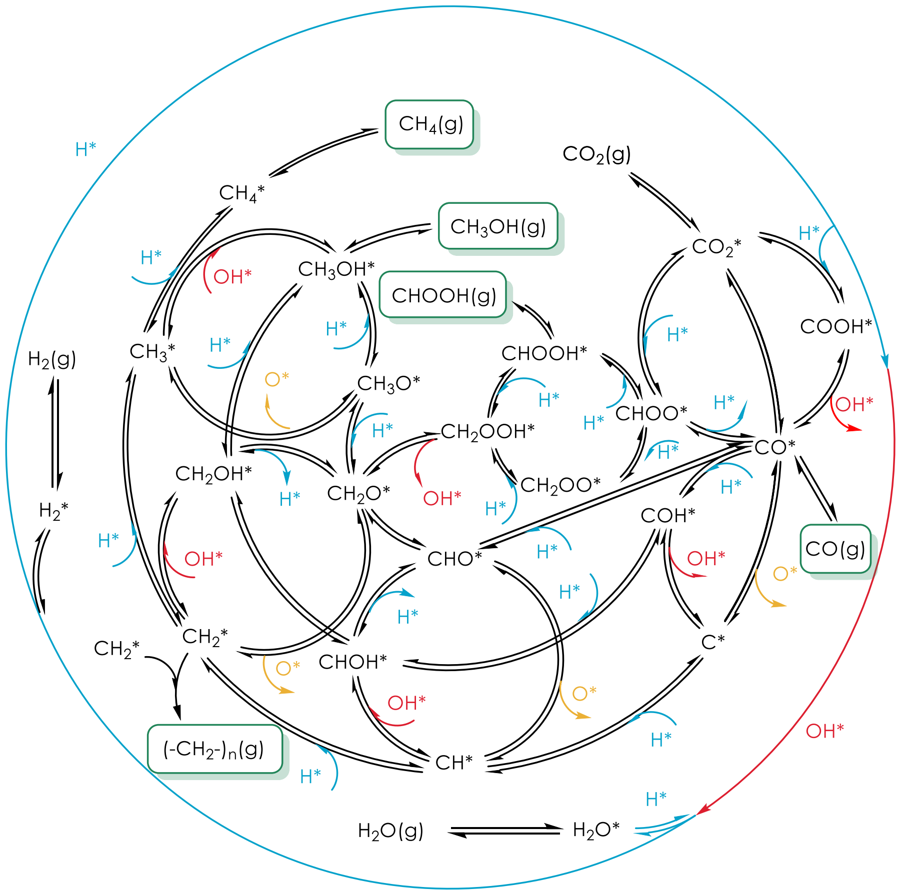
[a] Räuchle, K.; Plass, L.; Wernicke, H.-J.; Bertau, M.. *Energy Technology* **2016,** *4* (1), 193-200..

Methanol synthesis - Selectivity

Methanol Synthesis	(1) $CO + 2H_2 \rightleftharpoons CH_3OH$	$\Delta H°_{298} = -91$ kJ/mol	$\Delta G°_{298} = -25$ kJ/mol
	(2) $CO_2 + 3H_2 \rightleftharpoons CH_3OH + H_2O$	$\Delta H°_{298} = -50$ kJ/mol	$\Delta G°_{298} = +4$ kJ/mol
Reverse Water-Gas Shift	(3) $CO_2 + H_2 \rightleftharpoons CO + H_2O$	$\Delta H°_{298} = +42$ kJ/mol	$\Delta G°_{298} = +29$ kJ/mol
Sabatier Reaction	(4) $CO_2 + 4H_2 \rightleftharpoons CH_4 + 2H_2O$	$\Delta H°_{298} = -165$ kJ/mol	$\Delta G°_{298} = -131$ kJ/mol
Formic Acid Synthesis	(5) $CO_2 + H_2 \rightleftharpoons HCOOH$	$\Delta H°_{298} = -32$ kJ/mol	$\Delta G°_{298} = 33$ kJ/mol

GHENT UNIVERSITY

Methanol synthesis: Catalyst Design



	Cu/ZnO	Ni_5Ga_3[a]	[Ru][b]	Ru/LDH
Methanol Synthesis	✓	✓	✓	✗
Reverse water-gas shift	✓	✓	✗	✗
Sabatier reaction	✗	✗	✗	✗
Formic acid Synthesis	✓	✓	✓	✓

GHENT UNIVERSITY

[a] Nørskov, J. K *et al Nat. Chem.* **2014,** *6* (4), 320-324.
[b] Wesselbaum, S.; vom Stein, T.; Klankermayer, J.; Leitner, W. *Angew. Chem., Int. Ed. Engl.* **2012,** *51* (30), 7499-7502,

Methanol synthesis

Methanol Synthesis

(1) $CO + 2H_2 \rightleftharpoons CH_3OH$ ΔH°_{298} = -91 kJ/mol ΔG°_{298} = -25 kJ/mol

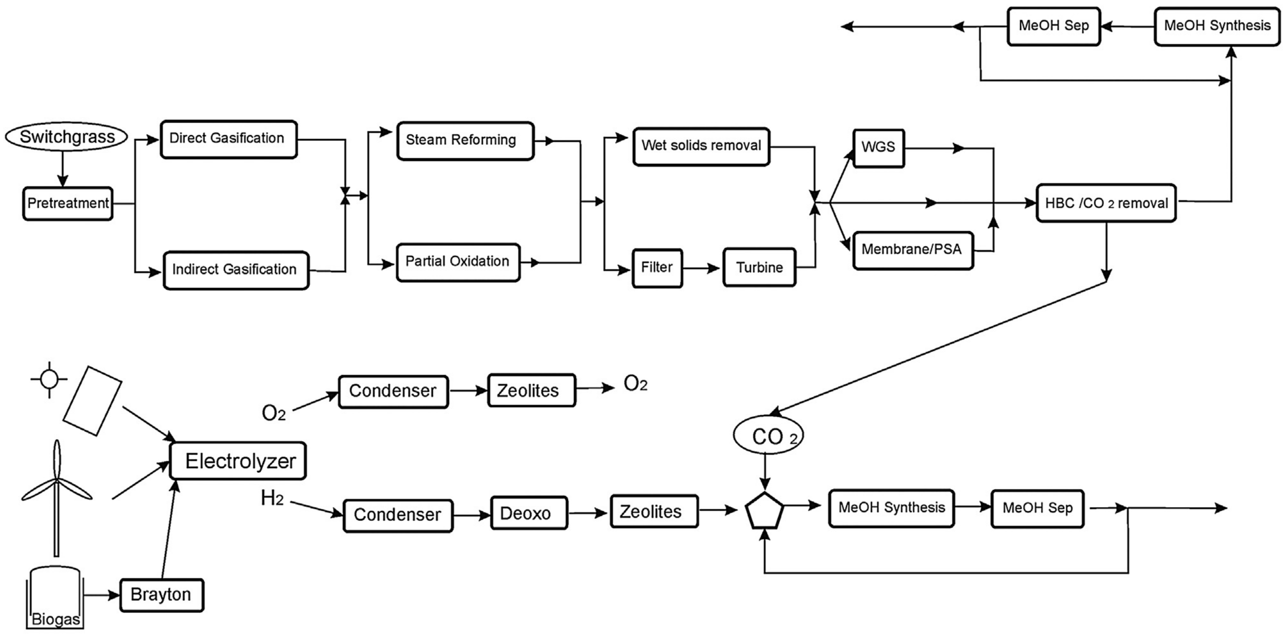
(2) $CO_2 + 3H_2 \rightleftharpoons CH_3OH + H_2O$ ΔH°_{298} = -50 kJ/mol ΔG°_{298} = +4 kJ/mol

Reverse Water-Gas Shift

(3) $CO_2 + H_2 \rightleftharpoons CO + H_2O$ ΔH°_{298} = +42 kJ/mol ΔG°_{298} = +29 kJ/mol

$H_2/CO_2/CO$/inert	P (Bar)	T (°C)	X_C %	Selectivity$_{CH3OH}$ %	Yield$_{CH3OH}$ %
60/0/**20**/20 **(CO)**	50	250	60	100	60
60/**20**/0/20 **(CO_2)**	50	250	25	63	**16**
60/20/0/20	50	**200**	34	94	32
60/20/0/20	50	**150**	51	100	51
60/20/0/20	**200**	250	54	96	52

Methanol: Bio-C and Solar H_2



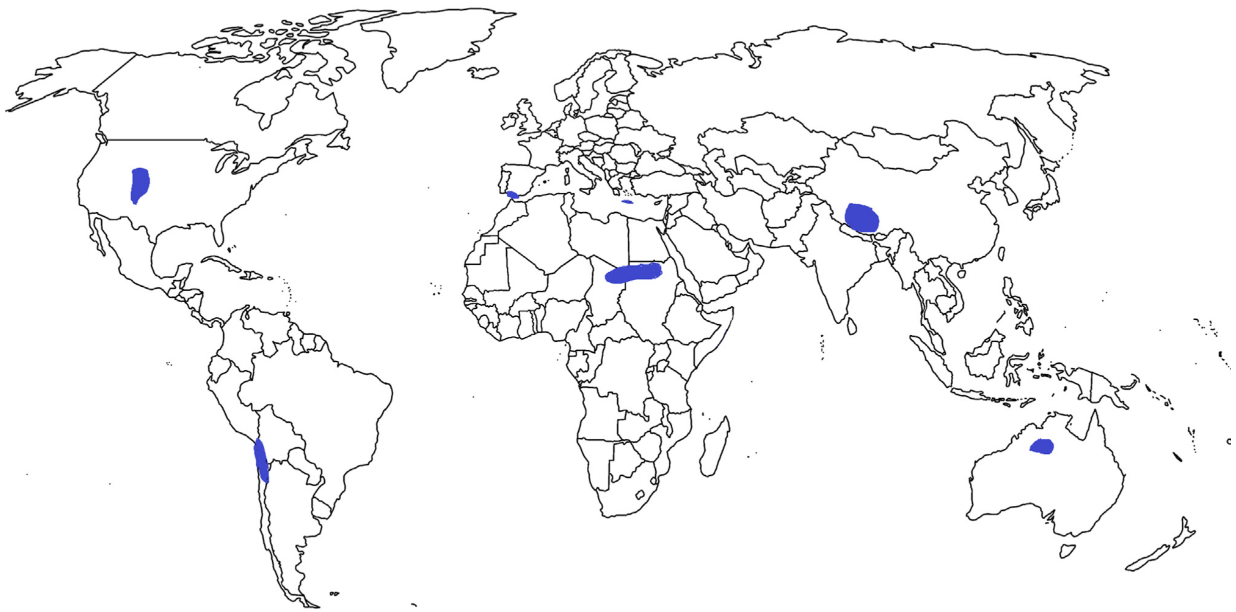


Fig. 6. Possible locations for the facility.

C from Biomass (gasification) and H_2 from PV/Wind - Electrolysis

Capacity: 1700 t/d switchgrass -> ~1700 t/d methanol

Price: $250-350/ton methanol

Investment: $1000M

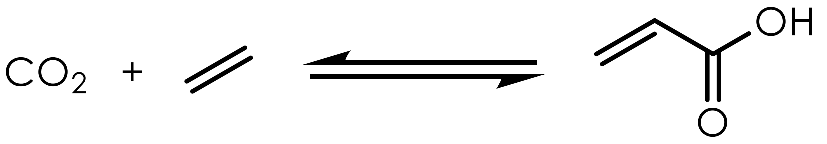
GHENT UNIVERSITY

Martin and Grossmann, Comp. and Chem. Eng. (2016), Similar concept: Rakesh Agrawal, 2009

Acrylates

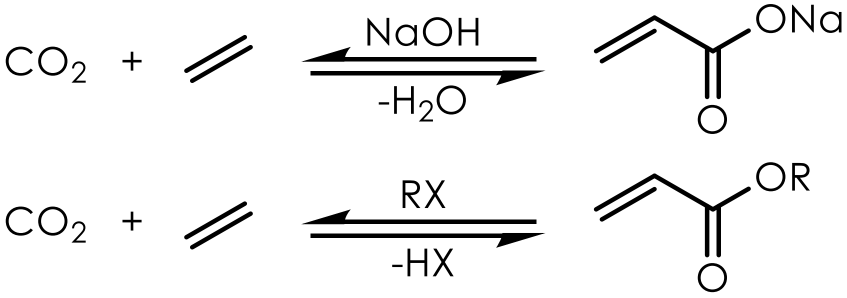
Early stage
Low TON
Use of stoichiometric bases

Acrylic Acid Synthesis



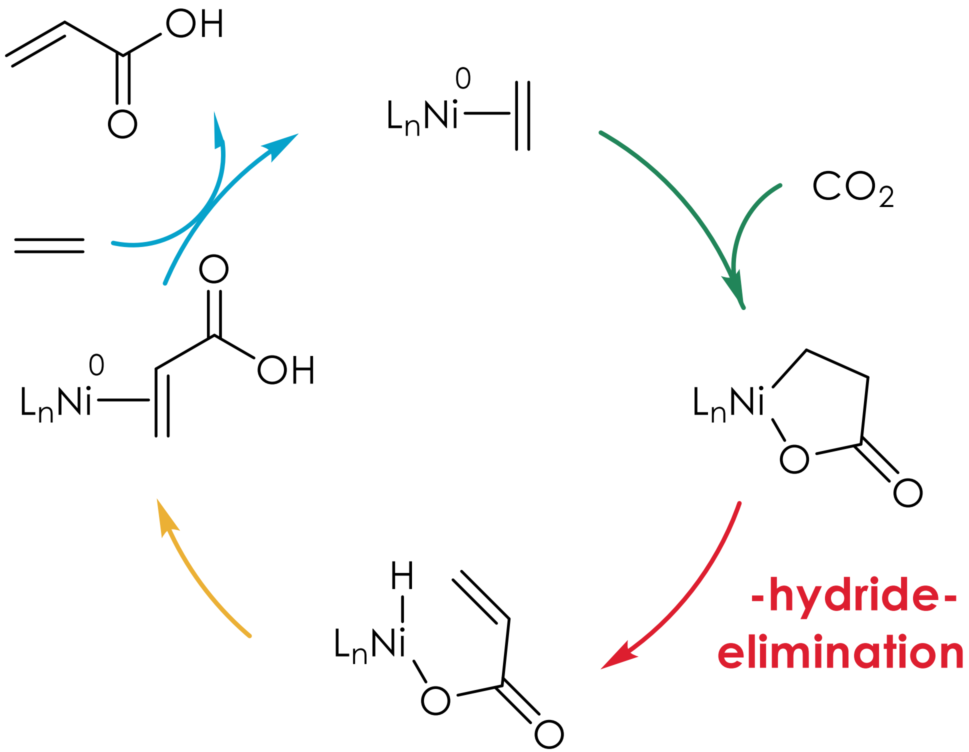
$\Delta G° = +43$ kJ/mol

Acrylate Synthesis



$\Delta G° = -56$ kJ/mol

$\Delta G° = +21$ kJ/mol



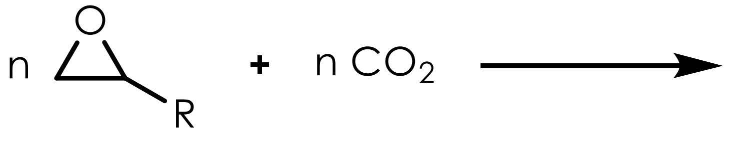
Large growing market: 5 million t/year[a]
Main ingredient for superabsorbent polymers
Immediate economic value

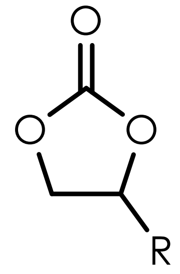
[a]D. Byrne, *IHS Chemical Bulletin* **2016**, 14-15

GHENT UNIVERSITY

Polyols for PUR

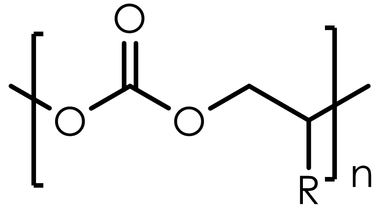
Main Challenge:
Selectivity





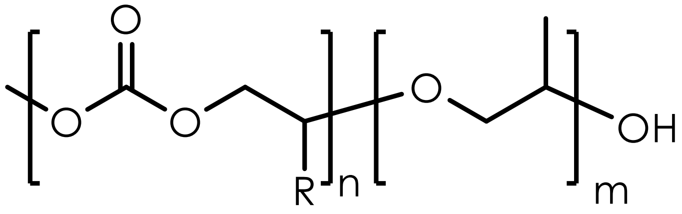
Solvent

Platform Chemical



High Mw Binder for Ceramics

Biodegradable/compostable



Low Mw

Polyols for PUR

Bayer’s Dream Process

Novomer

GHENT UNIVERSITY

CO_2 materials - Symbiosis

Sustainable Process Industry through Resource and Energy Efficiency

1 Separation and supply of carbon dioxide (CO_2)

CO_2 →

2 Processing of CO_2

Polyol →

3 Production of consumer products

Polyurethane

fossil resource depletion reduction:

↓ 13-16 %

GHENT UNIVERSITY

GHENT
UNIVERSITY

ACID RAIN

$\underline{S}O_2$

GHENT
UNIVERSITY

Conclusions - KVAB

A Carbon-free economy is unthinkable

Objective: CO_2-neutral society

Natural photosynthesis is too slow

to close the carbon cycle

Solar-driven chemical technology

needs to be implemented

GHENT UNIVERSITY

Need for a Positive Message?

Preserve carbon-based standard of living

Introduce CO_2 and Renewable Energy in the fuel and chemicals cycle